Atmospheric Pollution Research 6 (2015) 202-208

Atmospheric Pollution Research

www.atmospolres.com

Characteristics of carbonaceous aerosols in Beijing based on two–year observation

Zhongjun Xu [1], Tianxue Wen [2], Xingru Li [3], Jinggang Wang [1], Yuesi Wang [1,2]

[1] *Department of Environmental Science and Engineering, Beijing University of Chemical Technology, Beijing 100029, China*
[2] *State Key Laboratory of Atmospheric Boundary Layer Physics and Atmospheric Chemistry, Institute of Atmospheric Physics, Chinese Academy of Sciences, Beijing 100029, China*
[3] *Department of Chemistry, Analytical and Testing Center, Capital Normal University, Beijing 100048, China*

ABSTRACT

Both organic carbon (OC) and elemental carbon (EC) play an important role in climate change and human health. In the present work, OC and EC analysis was done for size segregated aerosols collected in Beijing during a period of two years (2009–2011). Both OC and EC concentrations exhibited a bimodal size distribution with the fine mode at 0.43–0.65 μm and the coarse mode at 4.7–5.8 μm. The carbonaceous species were prone to enrich in the fine particles, with 22.5±11.5 and 15.9±5.6 μg m^{-3} of OC and 2.7±1.5 and 1.1±0.7 μg m^{-3} of EC in the fine particles ($PM_{2.1}$) and the coarse particles ($PM_{>2.1}$), respectively. OC and EC accounted for 39.9% and 8.2%, respectively, of PM mass in <0.43 μm size range. The highest concentrations of carbonaceous species were noticed during winter. An increase in carbonaceous species between the two–year observations may be mainly attributed to the increasing vehicular exhaust in Beijing and the increasing emissions from coal combustion in neighboring provinces. The concentrations of secondary organic carbon (SOC) were the highest in $PM_{2.1}$ for winter and the lowest in $PM_{>2.1}$ for autumn. SOC averagely contributed to OC (56.5%) in the aerosols of Beijing during the two–year observation.

Keywords: *Organic carbon, elemental carbon, carbonaceous aerosols, Beijing*

Corresponding Author:
Zhongjun Xu
☎ : *+86-10-64427356*
🖷 : *+86-10-62082586*
✉ : *xuzj@mail.buct.edu.cn*

Article History:
Received: 04 April 2014
Revised: 08 September 2014
Accepted: 09 September 2014

doi: 10.5094/APR.2015.024

1. Introduction

In recent years, China suffered from serious air pollution problem particularly due to a large scale fossil fuel burning. For example, the coal consumption in China accounted for 50.2% (1 873.3 Mton) of the global coal consumption in 2012 (BP, 2013). Beijing, the capital of China, has more than 20 million inhabitants and 5.2 million motor vehicles after the industrialization and the urbanization over the last thirty years. Besides soot from coal combustion, traffic exhaust has been considered as an important contributor to particulate matter (PM) in Beijing**.** Although the local government makes efforts to reduce atmospheric pollutants, air pollution problem persists (Zhang et al., 2009). Carbonaceous aerosol is a major component of PM, accounting for 20–50% of atmospheric aerosols in heavily polluted atmospheres in urban areas (Duan et al., 2005). Carbonaceous aerosol is usually classified into organic carbon (OC), a light–scattering faction, and elemental carbon (EC), a light–absorbing faction. OC is a mixture of thousands of organic compounds such as polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs) and other hazardous components (Offenberg and Baker, 2000; Duan et al., 2005). OC is emitted directly from the primary sources, e.g., coal combustion, traffic exhaust and biomass burning, it also indirectly forms through gas–to–particle conversion processes of volatile organic compounds (VOCs) (Viidanoja et al., 2002; Niu et al., 2012). EC is also a mixture of graphite–like organic compounds and mainly originates from the incomplete combustion of carbonaceous fuels such as fossil and biomass fuels. Carbonaceous aerosol plays an important role in adverse health effects, visibility reduction, climate modulation, and chemical reactions in the atmosphere (Jacobson, 2001; Menon et al., 2002; Poschl, 2005; Mauderly and Chow, 2008). Therefore, information on the concentration and the distribution of carbonaceous aerosol in atmosphere is of great interest.

Studies on aerosol OC and EC in Beijing are reported by a large body of literature, which was involved in a change in OC and EC concentrations during one season (Duan et al., 2005; Zhang et al., 2009), or during several seasons (Yang et al., 2011; Zhao et al., 2013). Few works have focused on carbonaceous fraction of size–segregated aerosols in Beijing, although many studies demonstrated size distribution characteristics of aerosol OC and EC worldwide (Gnauk et al., 2008; Saarikoski et al., 2008; Kam et al., 2012; Pio et al., 2013). These reported findings illustrated that the mass concentration and the size distribution of carbonaceous aerosol both exhibited a significant temporal variation. Therefore, the detailed information on the concentration and the distribution of carbonaceous aerosol in Beijing is helpful for developing an effective measure for air pollution control. In this study, we investigated OC, EC and SOC in atmospheric PM of Beijing during a period of two years (2009–2011), and identified sources of carbonaceous aerosols in Beijing.

2. Material and Methods

2.1. Site description

Carbonaceous aerosol measurements were conducted at the Institute of Atmospheric Physics, Chinese Academy of Sciences in Haidian District, Beijing City, China (39°580´N, 116°220´E) (Figure 1). This site is located between the North Third Ring Road and the North Fourth Ring Road. The apparatus used in this study was installed on the roof of a two–story building (10 m above ground). An automated weather station was placed at a distance of 10 m from the sampler. Meteorological data on temperature, relative humidity and wind speed were recorded concurrently (Figure 2).

2.2. Aerosol sampling

Particle samples were collected using an Andersen sampler (Andersen Series 20–800, USA) equipped with quartz fiber filters of 47 mm in diameter at a flow rate of 28.3 L min^{-1}. At each sampling, aerosol particles have been collected for 24 h, starting from 08:00 LST to 08:00 LST. Particle samples were segregated into 9 size stages by the sampler: >9.0, 9.0–5.8, 5.8–4.7, 4.7–3.3, 3.3–2.1, 2.1–1.1, 1.1–0.65, 0.65–0.43 and <0.43 µm. All quartz fiber filters were pre–heated at 450 °C for 4 h to remove all organic matter and have been conditioned in a constant humidity desiccator (temperature: 25 °C, relative humidity: 50%) for 24 h before weighing. After the sampling, the filters were wrapped with aluminum foil and have been also conditioned in the same desiccator for 24 h. After weighing, the filters were stored in a freezer (–20 °C) prior to carbonaceous faction analysis. The particle sampling was carried out twice a month and 48 particle samples were taken from September 2009 to August 2011. However, 12 samples were damaged during the storage and could not be used in the analysis.

2.3. Sample analysis

The mass concentrations of size–segregated PM were obtained by subtracting the quartz fiber filters before sampling from the corresponding filters after sampling. The mass of each filter was weighed by a microbalance with a resolution of 1 µg.

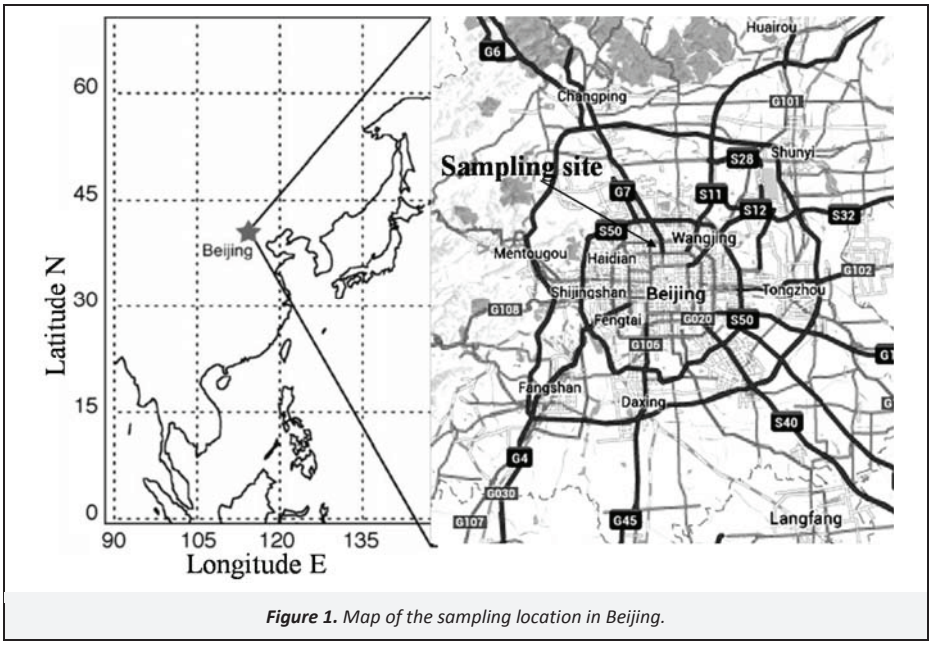

Figure 1. *Map of the sampling location in Beijing.*

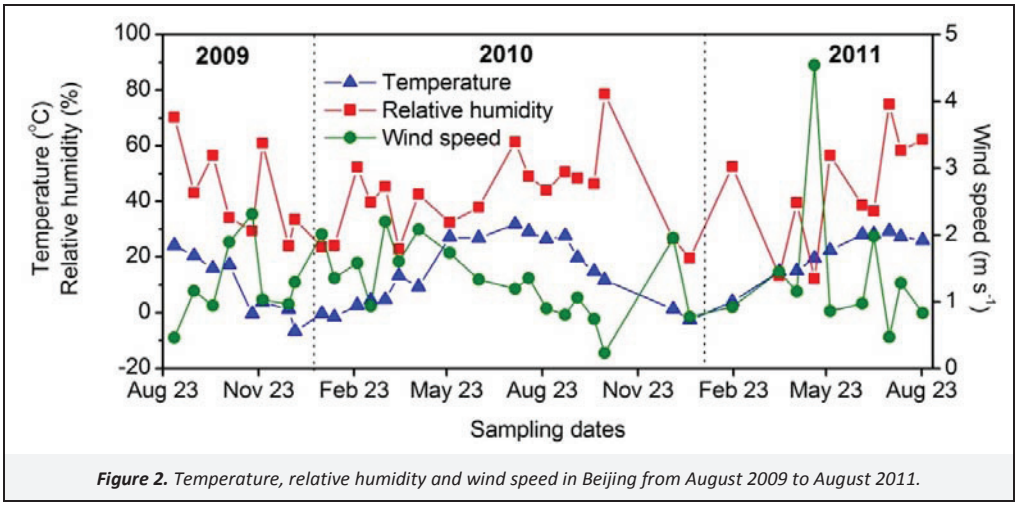

Figure 2. *Temperature, relative humidity and wind speed in Beijing from August 2009 to August 2011.*

OC and EC in aerosol samples were determined by a carbon analyzer (DRI Model 2001A, Desert Research Institute, USA) using the thermal optical reflection method. Firstly, a punched piece (0.495 cm^2) of a quartz fiber filter containing aerosol sample was heated stepwise up to 120 °C, 250 °C, 450 °C and 550 °C in a pure helium atmosphere for OC volatilization. Then the volatilized OC was converted into CO_2 via a manganese dioxide (MnO_2) catalyst. Subsequently, the residual aerosol sample was further heated stepwise up to 550 °C, 700 °C and 800 °C in a 2% oxygen–contained helium atmosphere for EC oxidation to CO_2. Finally, the produced CO_2 was catalytically converted to CH_4 by a Ni catalyst, and OC and EC were quantified by measuring the CH_4 with a flame ionization detector (FID). The OC–EC split was corrected as the laser transmittance returned to the initial value. The analyzer was calibrated using a standard mixture of CH_4 and CO_2 before and after sample analysis. One sample was selected at random from every 10 samples to carry out a duplicate analysis. The errors in the measurement presented here were less than 10% for TC (OC+EC). Blank filters were also analyzed to check any possible background contamination. Normally, OC and EC concentrations in the blank filters were less than 1% of the sample filters. The corrected OC and EC concentrations were obtained by subtracting the values in the blank filters from those in the samples. The detection limits for OC and EC on a quartz fiber filter are 0.82 and 0.20 μg cm^{-2}, respectively.

2.4. Statistical analysis

Data analysis was performed with SYSTAT for Windows (SPSS, Inc.). An analysis of variance (ANOVA) test was applied to test the differences of carbonaceous species in different seasons.

3. Results and Discussion

3.1. Temporal variations of PM, OC and EC

The temporal variations of size–segregated PM, OC and EC in the aerosols of Beijing from August 2009 to August 2011 are shown in Figure 3. PM, OC, and EC experienced significant variations during the two–year observation. The average concentration in fine particles ($PM_{2.1}$, 100.7±77.2 μg m^{-3}) was comparable with that in coarse particles ($PM_{>2.1}$, 126.7±70.2 μg m^{-3}) during the two years. Considering the Chinese Grade–II standards of 35 μg m^{-3} (annual average) for $PM_{2.5}$ (Ministry of Environmental Protection of the People's Republic of China, 2012), air pollution resulting from fine particles was serious in Beijing. The average OC concentrations in $PM_{2.1}$ and $PM_{>2.1}$ were 22.5±11.5 μg m^{-3} and 15.9±5.6 μg m^{-3} during the two years, respectively. The average EC concentrations in $PM_{2.1}$ and $PM_{>2.1}$ were 2.7±1.5 μg m^{-3} and 1.1±0.7 μg m^{-3} during the two years, respectively. The results indicated that carbonaceous species enriched more in fine particles than in coarse particles. The seasonal average concentrations of OC and EC distributed in $PM_{2.1}$ and $PM_{>2.1}$ are illustrated in Figure 4. During the two–year observation, OC concentrations in $PM_{2.1}$ followed the order of winter>autumn>summer>spring (P<0.05) while there was no significant difference of OC concentrations in $PM_{>2.1}$ among four seasons. The EC concentrations in both $PM_{2.1}$ and $PM_{>2.1}$ were significantly (P<0.05) higher in winter, respectively. In addition, there were inter–annual differences in OC and EC concentrations between the two–year observations. The average OC concentration tended to increase significantly (P<0.05) between the two winters and to decrease slightly between the other seasons, respectively. The average EC concentration in PM showed a systematic increase (P<0.05) between the two–year observations.

In Beijing, coal consumption dropped by 11.2%, from 26.65 million tons in 2009 to 23.66 million tons in 2011, while the motor vehicle population rose by 23.9%, from 4.02 million in 2009 to 4.98 million in 2011 (BMBS, 2013). Correspondingly, petroleum (gasoline, kerosene, and diesel oil) consumption increased by 11.1%, from 9.46 million tons in 2009 to 10.51 million tons in 2011 (BMBS, 2013). EC emissions are closely associated with carbonaceous fuel combustion. Thus, an increase in EC emissions between the two–year observations might be mainly attributed to the vehicular exhaust. Cheng et al. (2013) found that the vehicular emission contributed 27.0–50.5% to the total EC in $PM_{2.5}$. Besides, the introduction of carbonaceous pollutants from increasing coal consumption in neighboring provinces might partly contribute to the increasing EC emissions. For example, coal consumption in Hebei increased by 12.4%, from 235.15 million tons in 2009 to 264.33 million tons in 2011 (HPBS, 2013), while coal consumption in Tianjin increased by 27.7%, from 41.20 million tons in 2009 to 52.62 million tons in 2011 (TMBS, 2013). Similarly, the increasing vehicular exhausts in Beijing and the increasing emissions from coal consumption in neighboring provinces may result in a higher OC concentrations in the winter of 2010 than in the winter of 2009.

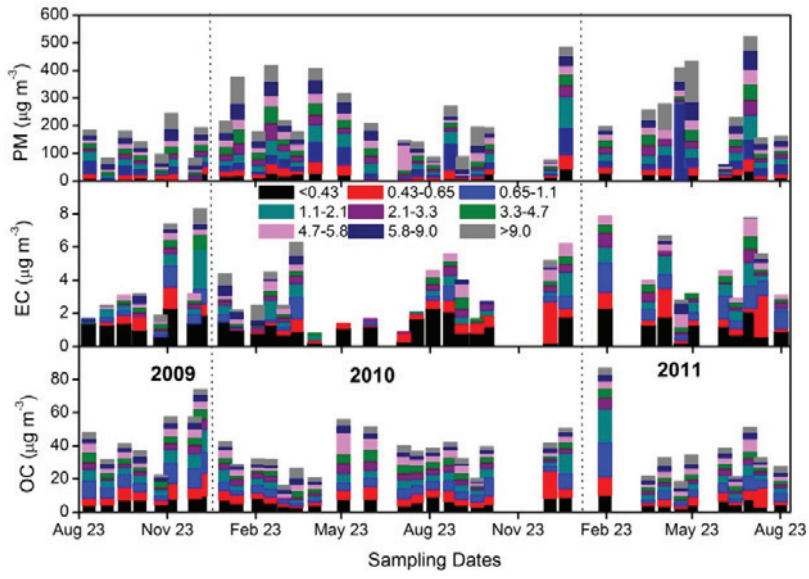

Figure 3. *PM, EC and OC concentrations in the size–segregated aerosols in Beijing during the two–year observation. Particle size displaying in the legend is based on μm.*

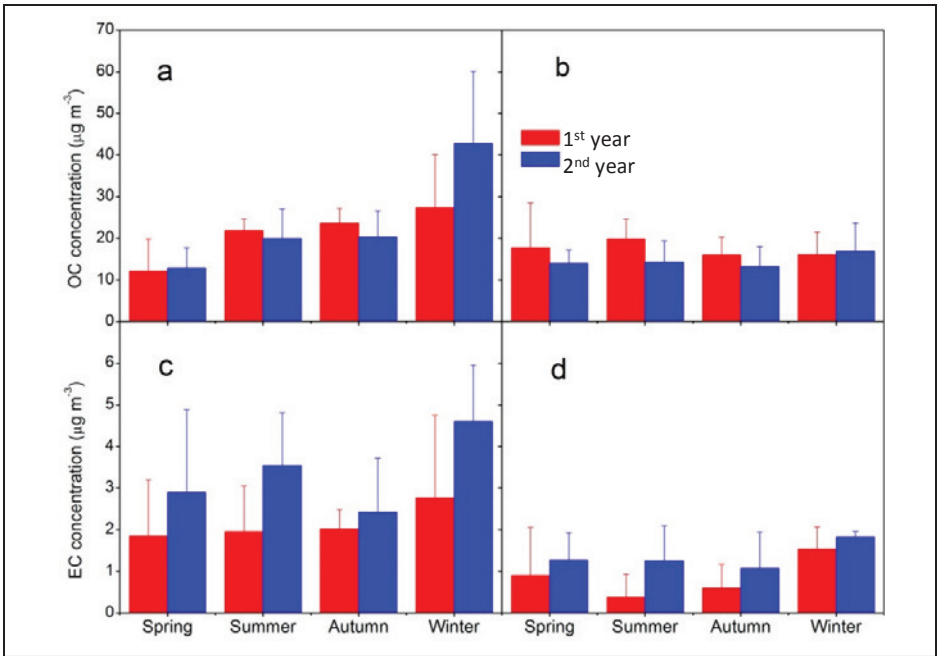

Figure 4. *The seasonal average concentrations of OC and EC distributed in $PM_{2.1}$ and $PM_{>2.1}$.* ***(a)*** *and* ***(b)*** *denote OC concentration in $PM_{2.1}$ and $PM_{>2.1}$,* ***(c)*** *and* ***(d)*** *denote EC concentration in $PM_{2.1}$ and $PM_{>2.1}$, respectively.*

The maximum concentrations of OC and EC in fine particles in Beijing occurred in winter and this trend agreed with the observations reported in a series of publications (He et al., 2001; Yang et al., 2010; Yang et al., 2011). Generally, a mass of coal is used as the fuel for domestic heating in a cold season in North China including Beijing, which leads to a sharp increase in the coal–related carbonaceous emission in this region (Yang et al., 2011). An isotopic signature study conducted in seven northern cities of China demonstrated that carbonaceous $PM_{2.5}$ in these regions is strongly impacted by coal combustion during winter (Cao et al., 2011). Besides, vehicular cold starts also significantly increase emissions of carbonaceous particles and their precursors (Singer et al., 1999). It should be noted that direct evidences further need to be provided to identify such speculative sources.

3.2. Size distributions of OC and EC

The size distributions of OC and EC were consistent, showing a bimodal pattern with a fine mode at 0.43–0.65 μm and a coarse mode at 4.7–5.8 μm (Figure 5). The size–segregated ratios of OC/PM and EC/PM on the basis of mass are presented in Figure 6. The ratios of OC/PM and EC/PM had a similar trend with the particle size. The contributions of OC and EC to PM were 39.9% and 8.2% in <0.43 μm size range, and substantially dropped to 16.9% and 1.3% in 0.65–1.1 μm size range, respectively. Thereafter, both contributions slowly decreased to 8.4% and 0.5% in >9.0 μm size range, respectively. OC includes a variety of hazardous organic materials, e.g., alkanes, PAHs and PCBs (Offenberg and Baker, 2000; Duan et al., 2005; Kong et al., 2010; Mirante et al., 2013). These hazardous organic materials associated with the fine particles are likely to be dispersed to a large area, being transported through the upper respiratory tract into the bronchiole and alveoli of the lungs where they pose a direct health risk (Chen et al., 1997). In recent years, severe air pollution episodes frequently occurred in Beijing, which has urged the local government to implement a series of measures to mitigate the air pollutant emissions, especially NO_X and SO_2. Considering that PM is reported to be the major air pollutant on about 90% of the days in Beijing (Chan and Yao, 2008) and a high percentage of carbonaceous species appear in PM, the primary and secondary sources of carbonaceous aerosols also need abating to improve the air quality.

3.3. Estimation of SOC concentrations

The direct separation of primary and secondary OC is difficult because OC is a complex mixture of many organic compounds with different chemical and physical properties (Chu, 2005). Nevertheless, several indirect approaches have been developed to estimate the amount of SOC concentrations (Turpin and Huntzicker, 1995; Castro et al., 1999; Strader et al., 1999). The EC tracer method was chosen in this study based on the OC and EC measurements. SOC can be calculated as follows:

$$SOC = OC - EC\left(\frac{OC}{EC}\right)_{min} \quad (1)$$

where, $(OC/EC)_{min}$ is the minimum of the OC/EC ratios (Turpin and Huntzicker, 1995; Castro et al., 1999). Equation (1) is also expressed as follows:

$$SOC = OC - POC = OC - (a + b\,EC) \quad (2)$$

where, a and b are the intercept and the slope, respectively. The product bEC is the primary OC associated with combustion sources (e.g., coal combustion, traffic) and the intercept a is considered to be the primary OC background concentration (Cao et al., 2007; Zhao et al., 2013). Parameters a and b are calculated by least–square regression using samples with the lowest 5–20% OC/EC ratios (Cao et al., 2007). In this study, parameters a and b were calculated using samples with the lowest 10% OC/EC ratios.

The seasonal variations of size–segregated SOC concentrations and SOC/OC ratios are illustrated in Figure 7, based on primary OC/EC ratios of 2.15 in spring, 3.99 in summer, 2.69 in autumn, and 4.22 in winter. By this estimate, SOC concentrations peaked at 0.65–1.1 μm size range in autumn and winter, and there was no obvious SOC peak in spring and summer.

SOC concentrations in $PM_{2.1}$ during winter were significantly (P<0.01) higher than those during other seasons while SOC

concentrations in $PM_{>2.1}$ during autumn were significantly (P<0.05) lower than those during other seasons. The highest SOC concentrations in the fine particles were also found during winter for several northern cities of China (Cao et al., 2007; Zhao et al., 2013). Overall, SOC/OC gradually rose with an increase in particle size (Figure 7). SOC accounted for (63.1±20.2)% of OC during spring, (59.2±13.9)% of OC during summer, (40.8±11.3)% of OC during autumn, and (63.1±13.1)% of OC during winter. On average, 56.5% of OC originated from SOC in the aerosols of Beijing during the two–year observation. Except that SOC/OC in $PM_{>2.1}$ during autumn was significantly (P<0.05) smaller than that during other seasons, there was no significant difference in SOC/OC during all seasons. The similar SOC/OC ratios in all seasons except autumn indicated that comparable gas–to–particle conversion rates of VOCs occurred in each season. Usually, photochemical oxidation is weaker in winter than that in other seasons. However, the stable atmosphere and the low temperature in winter facilitate the condensation or adsorption of VOCs in aerosols, which compensates SOC production by photochemical oxidation in other seasons (Yang et al., 2011; Zhao et al., 2013).

4. Conclusions

The measurement of size–segregated aerosol samples during the two years indicated that the concentrations of carbonaceous species in $PM_{2.1}$ (ca. 22.5 μg m^{-3} of OC and 2.7 μg m^{-3} of EC) were higher than those in $PM_{>2.1}$ (ca. 15.9 μg m^{-3} of OC and 1.1 μg m^{-3} of EC). Especially, OC and EC accounted for 39.9% and 8.2% of PM mass in <0.43 μm size range, respectively. Maximum concentrations of carbonaceous species occurred in winter and carbonaceous species increased between the two–year observations. OC and EC concentrations both exhibited a bimodal size distribution, peaking at 0.43–0.65 μm in fine mode and 4.7–5.8 μm in coarse mode. SOC concentrations were the highest in $PM_{2.1}$ for winter and the lowest in $PM_{>2.1}$ occurred for autumn. On the average, SOC accounted for 56.5% of OC in the aerosols of Beijing during the two–year observations. Taking into account the large percentage of carbonaceous species in the aerosols of Beijing, the sources of carbonaceous aerosols need to be controlled to improve the air quality in Beijing.

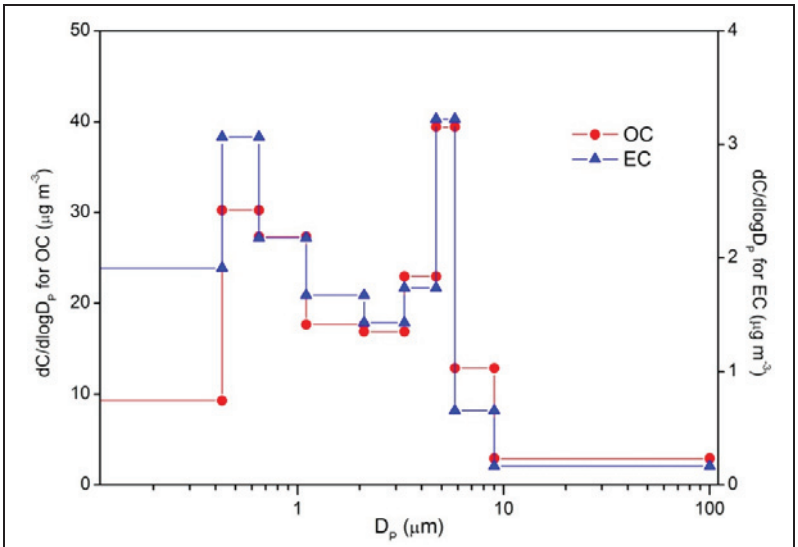

Figure 5. *The size distributions of EC and OC based on the two–year observed data.*

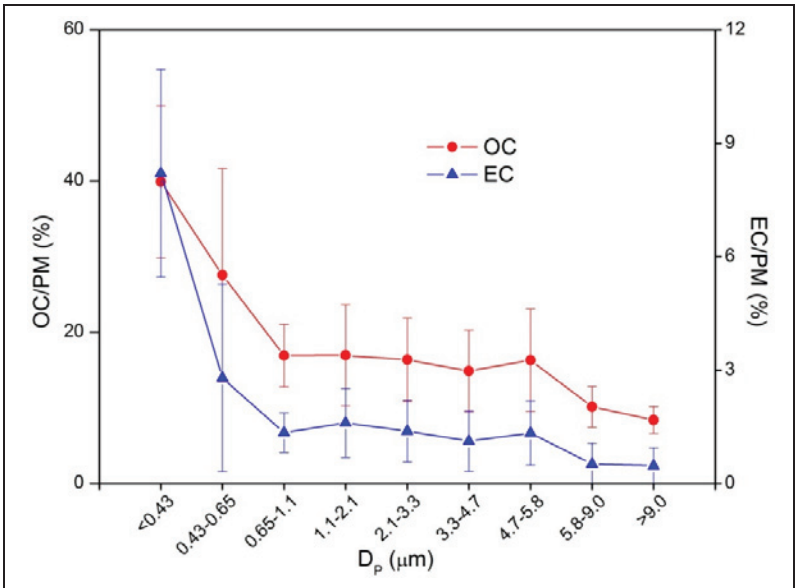

Figure 6. *The size–segregated proportions of EC and OC in PM on the basis of mass.*

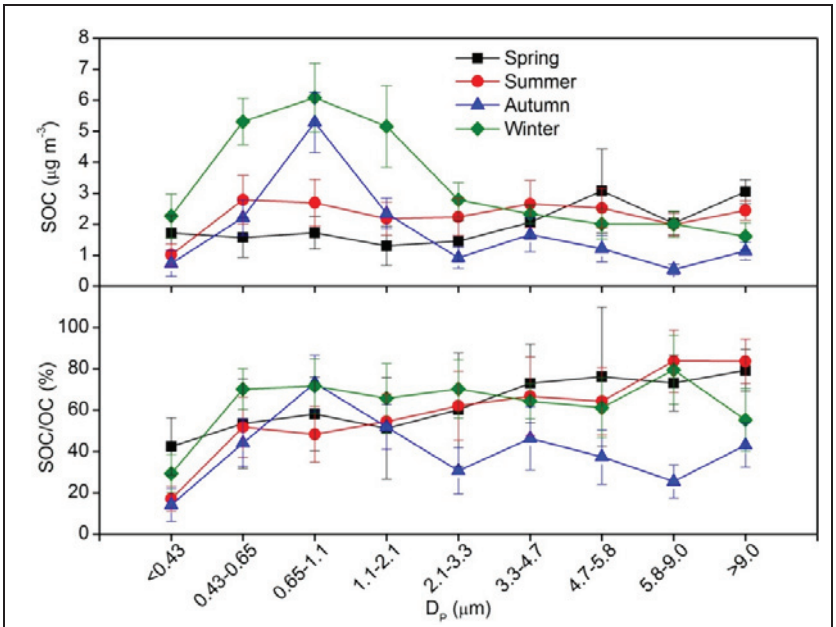

Figure 7. *Seasonal size–segregated SOC concentrations and SOC/OC ratios.*

Acknowledgments

This work was supported by the CAS Strategic Priority Research Program (No. XDA05100100), National Natural Science Foundation of China (No. 41230642), the CAS Strategic Priority Research Program (B) (No. XDB05020000) and the Fundamental Research Funds for the Central Universities (YS1401). We thank Dr. B. Hu for providing the meteorological data.

References

BMBS (Beijing Municipal Bureau of Statistics), 2013. Beijing Statistical Yearbook 2012, http://www.bjstats.gov.cn/nj/main/2012-tjnj/index.htm, accessed in 2014.

BP (British Petrol), 2013. BP Statistical Review of World Energy, www.bp.com/statisticalreview, accessed in 2014.

Cao, J.J., Chow, J.C., Tao, J., Lee, S.C., Watson, J.G., Ho, K.F., Wang, G.H., Zhu, C.S., Han, Y.M., 2011. Stable carbon isotopes in aerosols from Chinese cities: Influence of fossil fuels. *Atmospheric Environment* 45, 1359–1363.

Cao, J.J., Lee, S.C., Chow, J.C., Watson, J.G., Ho, K.F., Zhang, R.J., Jin, Z.D., Shen, Z.X., Chen, G.C., Kang, Y.M., Zou, S.C., Zhang, L.Z., Qi, S.H., Dai, M.H., Cheng, Y., Hu, K., 2007. Spatial and seasonal distributions of carbonaceous aerosols over China. *Journal of Geophysical Research–Atmospheres* 112, art. no. D22S11.

Castro, L.M., Pio, C.A., Harrison, R.M., Smith, D.J.T., 1999. Carbonaceous aerosol in urban and rural European atmospheres: Estimation of secondary organic carbon concentrations. *Atmospheric Environment* 33, 2771–2781.

Chan, C.K., Yao, X., 2008. Air pollution in mega cities in China. *Atmospheric Environment* 42, 1–42.

Chen, S.J., Liao, S.H., Jian, W.J., Lin, C.C., 1997. Particle size distribution of aerosol carbons in ambient air. *Environment International* 23, 475–488.

Cheng, S.Y., Lang, J.L., Zhou, Y., Han, L.H., Wang, G., Chen, D.S., 2013. A new monitoring–simulation–source apportionment approach for investigating the vehicular emission contribution to the $PM_{2.5}$ pollution in Beijing, China. *Atmospheric Environment* 79, 308–316.

Chu, S.H., 2005. Stable estimate of primary OC/EC ratios in the EC tracer method. *Atmospheric Environment* 39, 1383–1392.

Duan, F.K., He, K.B., Ma, Y.L., Jia, Y.T., Yang, F.M., Lei, Y., Tanaka, S., Okuta, T., 2005. Characteristics of carbonaceous aerosols in Beijing, China. *Chemosphere* 60, 355–364.

Gnauk, T., Muller, K., van Pinxteren, D., He, L.Y., Niu, Y.W., Hu, M., Herrmann, H., 2008. Size–segregated particulate chemical composition in Xinken, Pearl River Delta, China: OC/EC and organic compounds. *Atmospheric Environment* 42, 6296–6309.

He, K.B., Yang, F.M., Ma, Y.L., Zhang, Q., Yao, X.H., Chan, C.K., Cadle, S., Chan, T., Mulawa, P., 2001. The characteristics of $PM_{2.5}$ in Beijing, China. *Atmospheric Environment* 35, 4959–4970.

HPBS (Hebei Provincial Bureau of Statistics), 2013. Hebei Economic Yearbook 2012, http://www.hetj.gov.cn/hetj/tjsj/ndsj/101374627641041.html, accessed in 2014.

Jacobson, M.Z., 2001. Strong radiative heating due to the mixing state of black carbon in atmospheric aerosols. *Nature* 409, 695–697.

Kam, W., Liacos, J.W., Schauer, J.J., Delfino, R.J., Sioutas, C., 2012. Size–segregated composition of particulate matter (PM) in major roadways and surface streets. *Atmospheric Environment* 55, 90–97.

Kong, S.F., Ding, X.A., Bai, Z.P., Han, B., Chen, L., Shi, J.W., Li, Z.Y., 2010. A seasonal study of polycyclic aromatic hydrocarbons in $PM_{2.5}$ and $PM_{2.5-10}$ in five typical cities of Liaoning Province, China. *Journal of Hazardous Materials* 183, 70–80.

Mauderly, J.L., Chow, J.C., 2008. Health effects of organic aerosols. *Inhalation Toxicology* 20, 257–288.

Menon, S., Hansen, J., Nazarenko, L., Luo, Y.F., 2002. Climate effects of black carbon aerosols in China and India. *Science* 297, 2250–2253.

Mirante, F., Alves, C., Pio, C., Pindado, O., Perez, R., Revuelta, M.A., Artinano, B., 2013. Organic composition of size segregated atmospheric particulate matter, during summer and winter sampling campaigns at representative sites in Madrid, Spain. *Atmospheric Research* 132, 345–361.

Niu, Z.C., Zhang, F.W., Kong, X.R., Chen, J.S., Yin, L.Q., Xu, L.L., 2012. One–year measurement of organic and elemental carbon in size–segregated atmospheric aerosol at a coastal and suburban site in Southeast China. *Journal of Environmental Monitoring* 14, 2961–2967.

Offenberg, J.H., Baker, J.E., 2000. Aerosol size distributions of elemental and organic carbon in urban and over–water atmospheres. *Atmospheric Environment* 34, 1509–1517.

Pio, C., Mirante, F., Oliveira, C., Matos, M., Caseiro, A., Oliveira, C., Querol, X., Alves, C., Martins, N., Cerqueira, M., Camoes, F., Silva, H., Plana, F., 2013. Size–segregated chemical composition of aerosol emissions in an urban road tunnel in Portugal. *Atmospheric Environment* 71, 15–25.

Poschl, U., 2005. Atmospheric aerosols: Composition, transformation, climate and health effects. *Angewandte Chemie International Edition* 44, 7520–7540.

Saarikoski, S., Frey, A., Makela, T., Hillamo, R., 2008. Size distribution measurement of carbonaceous particulate matter using a low pressure impactor with quartz fiber substrates. *Aerosol Science and Technology* 42, 603–612.

Singer, B.C., Kirchstetter, T.W., Harley, R.A., Kendall, G.R., Hesson, J.M., 1999. A fuel–based approach to estimating motor vehicle cold–start emissions. *Journal of the Air & Waste Management Association* 49, 125–135.

Strader, R., Lurmann, F., Pandis, S.N., 1999. Evaluation of secondary organic aerosol formation in winter. *Atmospheric Environment* 33, 4849–4863.

TMBS (Tianjin Municipal Bureau of Statistics), 2013. Tianjin Statistical Yearbook 2012, http://www.stats–tj.gov.cn/article/sjfb/index.asp, accessed in 2014.

Turpin, B.J., Huntzicker, J.J., 1995. Identification of secondary organic aerosol episodes and quantitation of primary and secondary organic aerosol concentrations during SCAQS. *Atmospheric Environment* 29, 3527–3544.

Viidanoja, J., Kerminen, V.M., Hillamo, R., 2002. Measuring the size distribution of atmospheric organic and black carbon using impactor sampling coupled with thermal carbon analysis: Method development and uncertainties. *Aerosol Science and Technology* 36, 607–616.

Yang, F., Huang, L., Duan, F., Zhang, W., He, K., Ma, Y., Brook, J.R., Tan, J., Zhao, Q., Cheng, Y., 2011. Carbonaceous species in $PM_{2.5}$ at a pair of rural/urban sites in Beijing, 2005–2008. *Atmospheric Chemistry and Physics* 11, 7893–7903.

Yang, F.M., Brook, J., He, K.B., Duan, F.K., Ma, Y.L., 2010. Temporal variability in fine carbonaceous aerosol over two years in two megacities: Beijing and Toronto. *Advances in Atmospheric Sciences* 27, 705–714.

Zhang, R.J., Ho, K.F., Cao, J.J., Han, Z.W., Zhang, M.G., Cheng, Y., Lee, S.C., 2009. Organic carbon and elemental carbon associated with PM_{10} in Beijing during spring time. *Journal of Hazardous Materials* 172, 970–977.

Zhao, P.S., Dong, F., Yang, Y.D., He, D., Zhao, X.J., Zhang, W.Z., Yao, Q., Liu, H.Y., 2013. Characteristics of carbonaceous aerosol in the region of Beijing, Tianjin, and Hebei, China. *Atmospheric Environment* 71, 389–398.